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CYCLIC AND ISOTHERMAL OXIDATION BEHAVIOR  
AT 1100° AND 1200° C OF NICKEL -  
20-PERCENT-CHROMIUM, NICKEL -  
20-PERCENT-CHROMIUM - 3-PERCENT-MANGANESE,  
NICKEL - 20-PERCENT-CHROMIUM -  
3-PERCENT-SILICON, AND NICKEL -  
40-PERCENT-CHROMIUM ALLOYS

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16. Abstract Four alloys, Ni-20Cr, Ni-20Cr-3Mn, Ni-20Cr-3Si, and Ni-40Cr were cyclically oxidized at 1100° and 1200° C for up to 100 hours. Oxidation behavior was judged by sample thickness and weight change, metallography, diffraction, and microprobe analysis. The least attacked were Ni-40Cr and Ni-20Cr-3Si. The alloy Ni-20Cr-3Mn was much less attacked than Ni-20Cr, but more than the other alloys. The formation of Cr <sub>2</sub> O <sub>3</sub> accounted for the increased resistance of Ni-40Cr and Ni-20Cr-3Si, and the formation of MnCr <sub>2</sub> O <sub>4</sub> accounts for the improvement in Ni-20-Cr-3Mn over Ni-20Cr.					
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CYCLIC AND ISOTHERMAL OXIDATION BEHAVIOR AT 1100<sup>0</sup> AND 1200<sup>0</sup> C OF  
NICKEL - 20-PERCENT-CHROMIUM, NICKEL - 20-PERCENT-CHROMIUM -  
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CHROMIUM ALLOYS

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SUMMARY

Additions of 3 weight percent manganese (Mn) and 3 weight percent silicon (Si) were made to nickel - 20-weight-percent chromium (Ni-20Cr). These alloys, along with Ni-20Cr and nickel - 40-weight-percent chromium (Ni-40Cr), were oxidized for 100 1-hour cycles at 1100<sup>0</sup> C and fifty 1-hour cycles at 1200<sup>0</sup> C. Oxidation behavior was judged by sample weight and thickness change, metallography, X-ray diffraction, and electron microprobe analysis. These tests showed that Ni-40Cr and Ni-20Cr-3Si were similar in behavior and were the most oxidation resistant alloys. Nickel - 20-weight-percent chromium - 3-weight-percent manganese was not as oxidation resistant, especially at 1200<sup>0</sup> C. The Ni-20Cr alloy was far less oxidation resistant than any of the other alloys.

The Ni-40Cr and Ni-20Cr-3Si alloys relied on a protective layer of chromium sesquioxide (Cr<sub>2</sub>O<sub>3</sub>) for their oxidation resistance. A silicon dioxide (SiO<sub>2</sub>) layer was noted beneath the Cr<sub>2</sub>O<sub>3</sub> layer on the Ni-20Cr-3Si, but it apparently had only a second-order effect. The source of protection improvement of the Ni-20Cr-3Mn seemed to be due to the formation of a relatively adherent manganese chromite (MnCr<sub>2</sub>O<sub>4</sub>) layer at the metal-oxide interface.

INTRODUCTION

The nickel-chromium binary system has formed the basis for superalloys and heater materials for many years. Compositions near nickel - 20 weight percent-chromium can

be traced back to 1906 (ref. 1). Many studies (e. g., refs. 2 to 5) have been made on the isothermal oxidation of nickel-chromium alloys. In general, these investigators have found that when sufficient chromium is present in the alloys (i. e., approximately 20 wt. %) a protective scale of chromium sesquioxide ( $\text{Cr}_2\text{O}_3$ ) is formed, which results in low oxidation rates. At lower chromium concentrations a complex scale of nickel oxide ( $\text{NiO}$ ), nickel chromite ( $\text{NiCr}_2\text{O}_4$ ), and  $\text{Cr}_2\text{O}_3$  is formed which is less protective. In fact, binary composition near 15 weight percent chromium oxidize more rapidly than does pure nickel (ref. 2).

In addition to these studies, much work has been conducted to define the role of impurities in the oxidation process of nickel-chromium alloys. References 6 and 7 report extensive studies conducted in this area. These findings suggested that small amounts of silicon were beneficial and that manganese was detrimental to the oxidation of nickel-chromium heater alloys. Manganese seemed to be associated with the formation of manganese chromite ( $\text{MnCr}_2\text{O}_4$ ), but the mechanism associated with silicon was not defined. More recently, Sugiyama and Nakayama (ref. 8) found that an amorphous layer of silicon dioxide ( $\text{SiO}_2$ ) was formed at the oxide-metal interface of oxidized nickel-chromium alloys containing 0.5 to 1.0 weight percent silicon.

Douglass (ref. 9) has tried to define the role of silicon and manganese in the isothermal oxidation of nickel-chromium alloys. He cast nickel - 20-weight-percent chromium alloys containing 1 and 3 weight percent silicon and 1 and 3 weight percent manganese. He concluded, primarily from weight change data, that those alloys containing 3 percent manganese and those containing 3-percent silicon oxidized decidedly less than pure nickel-chromium. He also concluded that the 3-percent manganese alloy, which formed an adherent  $\text{MnCr}_2\text{O}_4$  layer at the oxide-metal interface, was superior to the 3-percent silicon alloy.

Most applications for superalloys and heater alloys involve cyclic oxidation. This is often more severe than isothermal oxidation because it causes spallation of the otherwise protective oxide layer. Therefore, an improvement in isothermal oxidation behavior must be accompanied by improvements in cyclic oxidation if practical benefits are to be realized. The purpose of this study was to see if the apparent improvement noted by Douglass was real and if it could also be realized during cyclic oxidation.

In this investigation the samples were oxidized for up to 100 cycles. Each cycle consisted of a 1-hour stand at temperature followed by at least 40 minutes of cooling. The test temperatures were  $1100^\circ$  and  $1200^\circ$  C. Isothermal tests were also run for comparison with Douglass (ref. 9). The compositions investigated were nickel - 20-weight-percent chromium, nickel - 20-weight-percent chromium - 3-weight-percent silicon, nickel - 20-weight-percent chromium - 3-weight-percent manganese, and nickel - 40-weight-percent chromium. It should be pointed out that 3 weight percent silicon is a much higher atomic percent (about 6) than 3 weight percent manganese (about 3). Un-

published data indicate, however, that the oxidation of Ni-Cr alloys is relatively insensitive to silicon levels above at least 2 atomic percent. The samples were examined with light microscopy, X-ray diffraction, and electron microprobe. The extent of oxidation was judged by the change in weight and metal thickness.

## MATERIALS AND PREPARATION

All alloys were melted in alumina crucibles and cast into zirconia molds under a partial pressure of argon ( $5000 \text{ N/m}^2$ ). Table I shows the chemical analyses of the cast materials. In general, the compositions are close to the expected values and quite low in impurity content.

The castings were hot rolled ( $1150^\circ \text{C}$ ) to a thickness of 0.25 centimeter and cut into specimens 1.9 centimeters by 2.2 centimeters. One-half of the specimens were ground on all sides, and the other half were mechanically polished to a 0.5-micrometer finish on the major surfaces and ground on the edges. Finally, the specimens were ultrasonically cleaned in trichloroethylene and rinsed in methanol.

## Test Procedures

Thickness measurements. - Before oxidation, metal thickness measurements were made on a line parallel to 1.9-centimeter edges and midway between them with a bench micrometer. Nine measurements were made on each sample at approximately 0.2-centimeter intervals with a precision of  $\pm 1$  micrometer. After exposure the samples were mounted in epoxy and sectioned at the line of measurements. After polishing and etching the samples were measured with a filar eyepiece at approximately the same nine positions. The measurements were made from scale-metal interface to scale-metal interface with a precision of  $\pm 1$  micrometer. After subtraction the differences were averaged, and the average was called alloy recession. The overall accuracy is close to  $\pm 5$  micrometers.

Isothermal oxidation test. - Isothermal oxidation was carried out at  $1100^\circ$  and  $1200^\circ \text{C}$  in still air for 100 hours. As shown schematically in figure 1, a continuously recording electrobalance was used for measuring the weight change (ref. 10). The accuracy of the apparatus was  $\pm 0.1$  milligram. The specimens were suspended by a thin quartz rod into the furnace's hot zone and by a platinum wire above the hot zone to the balance.

Cyclic oxidation test. - Cyclic oxidation was carried out at  $1100^\circ$  or  $1200^\circ \text{C}$  in still air for total times at temperature of 100 and 50 hours, respectively. The apparatus used is described more fully in reference 10. Each cycle consisted of 1 hour at temper-

ature followed by 40 minutes in room-temperature air. It took  $1\frac{1}{2}$  minutes for the specimens to reach the test temperature when inserted in the furnace; they reached  $1000^{\circ}\text{C}$  in 30 seconds. When withdrawn from the furnace, the specimens cooled to  $550^{\circ}\text{C}$  in 1 minute and reached room temperature in 7 minutes. As shown schematically in figure 2 the samples were automatically cycled in and out of the furnace by a pneumatic cylinder controlled by timers operating solenoid valves. The apparatus was equipped with individual spall collectors that were automatically positioned under each sample during the cooling portion of each cycle. Thus, spalled oxide could be collected and analyzed. The specimens were periodically weighed between cycles.

Other room temperature tests. - Both spalls and in situ oxides were examined by X-ray diffraction. Metallographic evaluations were made and electron microprobe analyses were performed on selected samples.

## RESULTS AND DISCUSSION

The alloys Ni-20Cr, Ni-40Cr, Ni-20Cr-3Mn, and Ni-20Cr-3Si were oxidized at  $1100^{\circ}$  and  $1200^{\circ}\text{C}$  for up to 100 hours both isothermally and cyclically. Thermal cycling consisted of 1 hour at temperature followed by 40 minutes of cooling in still air. In all cases both the ground and the polished samples gave nearly identical results, and no distinction will be made between the two conditions.

### Isothermal Oxidation Weight Change

At both  $1100^{\circ}$  and  $1200^{\circ}\text{C}$  the differences among the alloys are slight: about a 1.5-milligram-per-square-centimeter spread at  $1100^{\circ}\text{C}$  and about a 2.0-milligram-per-square-centimeter spread at  $1200^{\circ}\text{C}$  (figs. 3 and 4). At both temperatures Ni-20Cr gained the most weight and Ni-20Cr-3Si the least. The Ni-20Cr-3Mn alloy gained less than Ni-40Cr at  $1100^{\circ}\text{C}$  but more than Ni-40Cr at  $1200^{\circ}\text{C}$ .

Using weight change to assess oxidation resistance of chromium-containing alloys presents a problem in the interpretation of high-temperature results (refs. 11 and 12). This is due to the volatility of chromium oxides, especially  $\text{Cr}_2\text{O}_3$  (see X-ray diffraction results). Therefore, these results are used mainly for comparison with those of Douglass on the same materials (ref. 9). Fair agreement (within a factor of 2) between the present work and Douglass' was obtained.

## Cyclic Oxidation Weight Change

The cyclic oxidation exposures resulted in a much more severe attack that separated the alloy performance to a greater degree than the isothermal tests. At 1100° C (fig. 5) Ni-20Cr lost 20 times as much weight as Ni-20Cr-3Mn, and Ni-40Cr and Ni-20Cr-3Si lost slightly less than Ni-20Cr-3Mn. At 1200° C (fig. 6) the rankings were nearly the same, but the attack was so severe that the exposure was limited to 50 hours. The Ni-40Cr and Ni-20Cr-3Si alloys both lost about 10 milligrams per square centimeter, and the Ni-20Cr-3Mn and Ni-20Cr alloys lost 60 and 340 milligrams per square centimeter, respectively.

It is interesting to note that the alloys that gained more weight in the isothermal tests and hence had thicker scales were those alloys that suffered more spallation. While this result was expected from observations of samples cooled to room temperature following isothermal exposure, reference 13 indicates in a current review of data on scale exfoliation that cooling stresses are lessened by scale thickening. Thus, observation and theory are certainly at odds. It does show a need for more research into the theory of spalling.

As in the isothermal tests, loss of chromium oxides by vaporization limits the utility of weight change values. At these temperatures and in still air, equivalent  $\text{Cr}_2\text{O}_3$  loss could reach 0.01 milligram per square centimeter (ref. 11). However, a much bigger factor in this case is the spalling process. Here weight losses (rather than weight gains) are the rule. This is primarily due to the spallation of the protective oxide layer followed by rapid growth and more spallation. One must remember that the weight changes measured are from room temperature weights at the end of a cycle. Therefore, the measured weight change equals the amount of oxide spall and vaporization less the amount of retained scale. The uncertainty lies in the amount of oxide remaining on the surface of the metal. One could visualize so much oxide forming that enough remains after spallation to give a net weight loss of zero. In general, this seldom happens, and a reasonable approximation of attack can be gained from weight loss data. To gain greater confidence, however, a metallographic evaluation of the oxide and thickness measurements should be made.

## Thickness Measurements

The alloy recession data are presented in figures 7 and 8. They confirm the weight-change data rankings at 1100° C and, within the  $\pm 5$ -micrometer estimate of error, Ni-20Cr-3Mn, Ni-20Cr-3Si, and Ni-40Cr had the same alloy recession, with the cyclic recessions being between one and a half and two times greater than the isothermal data. The Ni-20Cr recessions are about four times greater isothermally, but 20 times greater

cyclically. These data agree well with the weight change data, indicating that vaporization is not a major effect compared with spalling.

At 1200° C the isothermal rankings are the same as at 1100° C. The cyclic data are slightly different. The alloys Ni-20Cr-3Si and Ni-40Cr oxidize to the same extent, while Ni-20Cr-2Mn and Ni-20Cr oxidize about six and 30 times more, respectively. Also, compared with Ni-20Cr, thickness change results showed that the Ni-40Cr and the Ni-20Cr-3Si are 24 times more oxidation resistant to cyclic oxidation at 1100° C and 25 times more resistant at 1200° C. Similarly, with the 3-percent-manganese addition, improvements of 17 times at 1100° C and five times at 1200° C were achieved. The important points made by these data are twofold: (1) Both silicon and manganese increase the oxidation resistance, with silicon having a greater effect, and (2) Ni-20Cr-3Si oxidizes at about the same rate as Ni-40Cr both isothermally and cyclically.

### Metallography, X-ray Diffraction, and Microprobe

In this section mostly 1200° C data will be discussed. This has been done because, except where noted, the oxide morphology and compositions are the same at 1100° and 1200° C.

In cross section the oxide layer formed on Ni-20Cr (fig. 9(a)) after 100 hours of isothermal oxidation at 1200° C appears to be a single oxide  $\text{Cr}_2\text{O}_3$  with some internal oxidation. The microprobe data on the same sample (fig. 10), however, indicates a thin nickel-rich layer on the surface. X-ray diffraction (table II) shows the layer to be the NiO and establishes that there is also  $\text{NiCr}_2\text{O}_4$ , a spinel, probably at the NiO- $\text{Cr}_2\text{O}_3$  interface.

The same alloy after cyclic oxidation for 50 hours at 1200° C gives a more complex, multilayer oxide (figs. 11(a) and 12). X-ray diffraction (table II) again shows NiO,  $\text{NiCr}_2\text{O}_4$ , and  $\text{Cr}_2\text{O}_3$ ; however, there appears to be a substantial increase in the amount of NiO and  $\text{NiCr}_2\text{O}_4$  present. Very little internal oxidation was noted.

Both the cyclically and isothermally exposed Ni-20Cr-3Mn samples had a complex oxide (figs. 9(b), 11(b), 13, and 14). As in the case of Ni-20Cr, internal oxidation was noted only after isothermal exposure. This is probably due to the very rapid consumption of metal in this material. The interpretation of microprobe data (fig. 13) and X-ray data (table II) gives a straightforward indication of the oxide layer composition starting from the metal:  $\text{MnCr}_2\text{O}_4$ ,  $\text{Cr}_2\text{O}_3$ , and (Mn,Ni) $\text{Cr}_2\text{O}_4$ . The data from the cyclic testing indicate only a jumbled arrangement of spinels,  $\text{Cr}_2\text{O}_3$ , and NiO.



## General Discussion

The Ni-20Cr-3Si and Ni-40Cr data can be considered together both cyclically and isothermally (figs. 9(c) and (d), 11(c) and (d), and 15 to 18 and table II). Both alloys form a distinct  $\text{Cr}_2\text{O}_3$  layer on the surface. Both have internal oxidation, more after cyclic exposure than isothermal. The difference between the two alloys lies in the presence of a layer of  $\text{SiO}_2$  that exists beneath the  $\text{Cr}_2\text{O}_3$  layer in the Ni-20Cr-3Si sample. Note that the  $\text{SiO}_2$  layer is not continuous after isothermal exposure (fig. 9(c)). Silicon dioxide is present as an  $\alpha$ -cristobolite in the  $1200^\circ\text{C}$  samples but is assumed to be amorphous in the  $1100^\circ\text{C}$  samples (ref. 8). Such a discontinuous layer is probably not an effective diffusion barrier.

In general, the isothermal test results do not differ substantially from those obtained by Douglass (ref. 9). The Ni-20Cr-3Mn structures indicate that the inner layer of  $\text{MnCr}_2\text{O}_4$  is not as adherent as was hoped by Douglass (ref. 9). It does, however, reduce the rate of NiO and  $\text{NiCr}_2\text{O}_4$  formation as postulated by Armijo (ref. 14). In addition, a comparison of  $\text{Cr}_2\text{O}_3$  thicknesses on Ni-40Cr with Ni-20Cr-3Si, indicates that there is no substantial reduction in the growth rate of  $\text{Cr}_2\text{O}_3$  by silicon addition. These observations are consistent with the weight and metal thickness changes already noted. The results of cyclic testing do differ from Douglass (ref. 9) in that 3 percent silicon is clearly superior to 3 percent manganese.

## CONCLUDING REMARKS

Additions of 3 weight percent silicon and 3 weight percent manganese can substantially improve the oxidation resistance of Ni-20Cr under both isothermal and cyclic conditions at  $1100^\circ\text{C}$  and  $1200^\circ\text{C}$ . This is especially true in cyclic oxidation. In all cases the silicon offers a greater improvement than manganese; however, the advantage of silicon is substantial only during cyclic oxidation at  $1200^\circ\text{C}$ .

The silicon additions, which lead to the more oxidation resistant alloy, suppress the formation of NiO and  $\text{NiCr}_2\text{O}_4$  so that they never form even under the most severe test conditions. This alloy formed only  $\text{SiO}_2$  and  $\text{Cr}_2\text{O}_3$ . The role of the  $\text{SiO}_2$  is not fully understood, nor has the optimum silicon content been established. The usual view of such a system is that both NiO and  $\text{Cr}_2\text{O}_3$  are nucleated at the start of oxidation. Patches of each oxide grow laterally, and the oxide that covers the surface first controls further oxidation. Since NiO is known to grow faster than  $\text{Cr}_2\text{O}_3$ , it will dominate until enough  $\text{Cr}_2\text{O}_3$  nucleates to prevent this. This could result from having much more chromium in the alloy as in the Ni-40Cr. However, other mechanisms are possible. More nucleation sites could be present as at scratches and grain boundaries, or the rate

of growth of the NiO could be slowed. The slower rate of growth mechanism seems more probable to the author. Whichever mechanism holds, however, it allows the more stable  $\text{Cr}_2\text{O}_3$  to become the exclusive oxide at high chromium concentrations, that is, Ni-40Cr.

The mechanism of improvement afforded by manganese appears to be the formation of  $\text{MnCr}_2\text{O}_4$  at the expense of NiO and  $\text{NiCr}_2\text{O}_4$ . The manganese spinel apparently forms at a lower rate (ref. 13) and is more adherent than a NiO- $\text{NiCr}_2\text{O}_4$ - $\text{Cr}_2\text{O}_3$  scale leading to much reduced spalling in cyclic oxidation. Here is a case where a spinel is protective. It must be emphasized that it is protective as compared with a mixed layer of NiO,  $\text{NiCr}_2\text{O}_3$ , and  $\text{Cr}_2\text{O}_3$  - not as compared with  $\text{Cr}_2\text{O}_3$  alone.

Thus, the inherent tendency of a given oxide to spall has not been reduced by alloying the Ni-20Cr with silicon or manganese. These additions have controlled and slowed the growth of the oxide layers and their composition. These factors have in turn led to the reduced spalling.

## SUMMARY OF RESULTS

In this study the rankings of the alloys were the same isothermally and cyclically. However, the differences among the alloys were much greater under cyclic test conditions than under isothermal conditions.

This work deals with the effect of 3 weight percent silicon (Si) and 3 weight percent manganese (Mn) on the cyclic oxidation of nickel - 20-weight-percent chromium (Ni-20Cr) in air at  $1100^\circ$  and  $1200^\circ$  C. The oxidation behavior of these alloys along with that of nickel - 40-weight-percent chromium (Ni-40Cr) was judged by weight change, metal thickness loss, X-ray diffraction, metallography, and microprobe analyses. The major findings were as follows:

1. In general, cyclic exposure confirmed the isothermal rankings of the alloys.
2. An alloy with a 3-weight-percent addition of silicon to Ni-20Cr was slightly more resistant to cyclic oxidation than the Ni-20Cr-3Mn alloy at  $1100^\circ$  C and was more than five times better at  $1200^\circ$  C. This alloy was 24 times more resistant to cyclic oxidation than Ni-20Cr at  $1100^\circ$  C and 25 times more resistant at  $1200^\circ$  C.
3. The improvement in oxidation found by the addition of silicon was associated with an increased tendency for protective chromium sesquioxide ( $\text{Cr}_2\text{O}_3$ ) formation and a silicon dioxide ( $\text{SiO}_2$ ) layer beneath the  $\text{Cr}_2\text{O}_3$  layer. At  $1100^\circ$  C the  $\text{SiO}_2$  is amorphous, and at  $1200^\circ$  C it was an  $\alpha$ -cristobolite. In this case the  $\text{SiO}_2$  apparently plays a secondary role.
4. The cyclic and isothermal oxidation resistance of Ni-40Cr was the same as Ni-20Cr-3Si, caused by the formation of a protective  $\text{Cr}_2\text{O}_3$  layer.

5. Three-weight-percent additions of manganese to Ni-20-weight-percent chromium improved the cyclic oxidation of the alloy by 17 times at 1100° C and by five times at 1200° C based on metal thickness change.

6. The improvement in oxidation resistance by the addition of manganese was associated with the formation of an adherent, protective layer of manganese spinel ( $\text{MnCr}_2\text{O}_4$ ).

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National Aeronautics and Space Administration,  
Cleveland, Ohio, March 2, 1973,  
501-01.

## REFERENCES

1. Rentz, W. A.; and Donachie, M. J., Jr.: Oxidation and Sulfidation Corrosion of Nickel Base Superalloys. Tech. Rep. C6-18.5, ASM, Oct. 1966.
2. Barrett, C. A.; Evans, E. B.; and Baldwin, W. M., Jr.: High Temperature Scaling of Ni-Cr, Fe-Cr, Cu-Cr, and Cu-Mn Alloys. Tech. Rep. 3, Case Inst. Tech., Dec. 1955.
3. Birks, N.; and Rickert, H.: The Oxidation Mechanism of Some Nickel-Chromium Alloys. J. Inst. Metals, vol. 91, 1962-1963, pp. 308-311.
4. Wood, G. C.; Hodgkiess, T.; and Whittle, D. P.: A Comparison of the Scaling Behaviour of Pure Iron-Chromium and Nickel-Chromium Alloys in Oxygen. Corrosion Sci., vol. 6, no. 3/4, 1966, pp. 129-147.
5. Giggins, C. S.; and Pettit, F. S.: Oxidation of Ni-Cr Alloys Between 800° and 1200° C. Trans. AIME, vol. 245, no. 12, Dec. 1969, pp. 2495-2507.
6. Hickman, J. W.; and Gulbransen, E. A.: An Electron Diffraction Study of Oxide Films Formed on Nickel-Chromium Alloys. Trans. AIMME, vol. 180, 1949, pp. 519-533.
7. Gulbransen, Earl A.; and Andrew, Kenneth F.: Oxidation Studies on the Nickel-Chromium and Nickel-Chromium-Aluminum Heater Alloys. J. Electrochem. Soc., vol. 106, no. 11, Nov. 1959, pp. 941-948.
8. Sugiyama, Masataka; and Nakayama, Tadayuki: Effect of Silicon on High-Temperature Oxide Films in Heat-Resistant Alloys. Japan Inst. Metals J., vol. 24, Aug. 1960, pp. 541-544.

9. Douglass, D. L.; and Armijo, J. S.: The Effect of Silicon and Manganese on the Oxidation Mechanism of Ni-20 Cr. *Oxidation of Metals*, vol. 2, no. 2, 1970, pp. 207-231.
10. Santoro, Gilbert J.; Deadmore, Daniel L.; and Lowell, Carl E.: Oxidation of Alloys in Nickel-Aluminum System with Third Element Additions of Chromium, Silicon, and Titanium at 1100<sup>0</sup> C. NASA TN D-6414, 1971.
11. Hagel, William C.: Factors Controlling the High-Temperature Oxidation of Chromium. *ASM Trans.*, vol. 56, no. 3, Sept. 1963, pp. 583-599.
12. Kohn, Fred J.; and Sterns, Carl A.: Vaporization of Chromium Oxides from the Surface of TD-NiCr under Oxidizing Conditions. NASA TM X-52879, 1970.
13. Douglass, D. L.: Exfoliation and the Mechanical Behavior of Scales. *Oxidation of Metals and Alloys*. ASM, 1971, pp. 137-156.
14. Armijo, J. S.: Mechanisms and Kinetics of Nickel Chromite and Cobalt Chromite Spinel Formation. Stanford Research Inst. (NASA CR-72537), May 1969.

TABLE I. - CHEMICAL ANALYSIS

(a) Wet analysis

Nominal composition, wt. %	Analyzed composition, wt. % (at. %)
Ni-20Cr	Ni-19.9(21.9)Cr
Ni-20Cr-3Mn	Ni-19.5(21.4)Cr-2.5(2.6)Mn
Ni-20Cr-3Si	Ni-19.9(21.2)Cr-3.0(5.9)Si
Ni-40Cr	Ni-38.7(41.6)Cr

(b) Qualitative spectrographic analysis<sup>a</sup>

Element	Alloy (b)			
	Ni-20Cr	Ni-40Cr	Ni-20Cr-3Mn	Ni-20Cr-3Si
Ni	VS	VS	VS	VS
Cr	S	S	S	S
Si	FT	VW	FT	M
Mn	FT	FT	M	FT
Al	T	FT	T	VW
Fe	FT	T	FT	T
Mo	FT	ND	VW	FT
Mg	T	VW	FT	FT

<sup>a</sup>The elements B, Co, Hf, Nb, Pt, Ta, Th, Ti, V, Y, Zn, and Zr were looked for but were not detected.

<sup>b</sup>Ratings: Very strong, VS; strong, S; medium, M; very weak, VW; trace, T; faint trace, FT; and not detected, ND.

TABLE II. - SUMMARY OF X-RAY DIFFRACTION DATA

[In all cases of in situ analysis nickel solid solution was also found. Phases are listed with strongest pattern first.]

Type of oxidation	Exposure, temperature, °C	Time	Alloy			
			Ni-20Cr	Ni-40Cr	Ni-20Cr-3Mn	Ni-20-Cr-3Si
			Oxides identified			
Isothermal	1100	100	NiO	Cr <sub>2</sub> O <sub>3</sub>	<sup>a</sup> (Ni, Mn)Cr <sub>2</sub> O <sub>4</sub>	Cr <sub>2</sub> O <sub>3</sub>
			Cr <sub>2</sub> O <sub>3</sub>		Cr <sub>2</sub> O <sub>3</sub>	
			<sup>a</sup> NiCr <sub>2</sub> O <sub>4</sub>			
Cyclic	1200	50	NiO	Cr <sub>2</sub> O <sub>3</sub>	(Ni, Mn)Cr <sub>2</sub> O <sub>4</sub>	<sup>b</sup> SiO <sub>2</sub>
			Cr <sub>2</sub> O <sub>3</sub>		Cr <sub>2</sub> O <sub>3</sub>	Cr <sub>2</sub> O <sub>3</sub>
			NiCr <sub>2</sub> O <sub>4</sub>		NiO	
	1100	100	NiO	Cr <sub>2</sub> O <sub>3</sub>	NiO	Cr <sub>2</sub> O <sub>3</sub>
			Cr <sub>2</sub> O <sub>3</sub>		(Ni, Mn)Cr <sub>2</sub> O <sub>4</sub>	NiCr <sub>2</sub> O <sub>4</sub>
			NiCr <sub>2</sub> O <sub>4</sub>		Cr <sub>2</sub> O <sub>3</sub>	
	1200	50	NiO	Cr <sub>2</sub> O <sub>3</sub>	NiO	Cr <sub>2</sub> O <sub>3</sub>
			NiCr <sub>2</sub> O <sub>4</sub>		(Ni, Mn)Cr <sub>2</sub> O <sub>4</sub>	SiO <sub>2</sub>
			Cr <sub>2</sub> O <sub>3</sub>		Cr <sub>2</sub> O <sub>3</sub>	

<sup>a</sup>Spinel structure.

<sup>b</sup>An α-crystobalite.

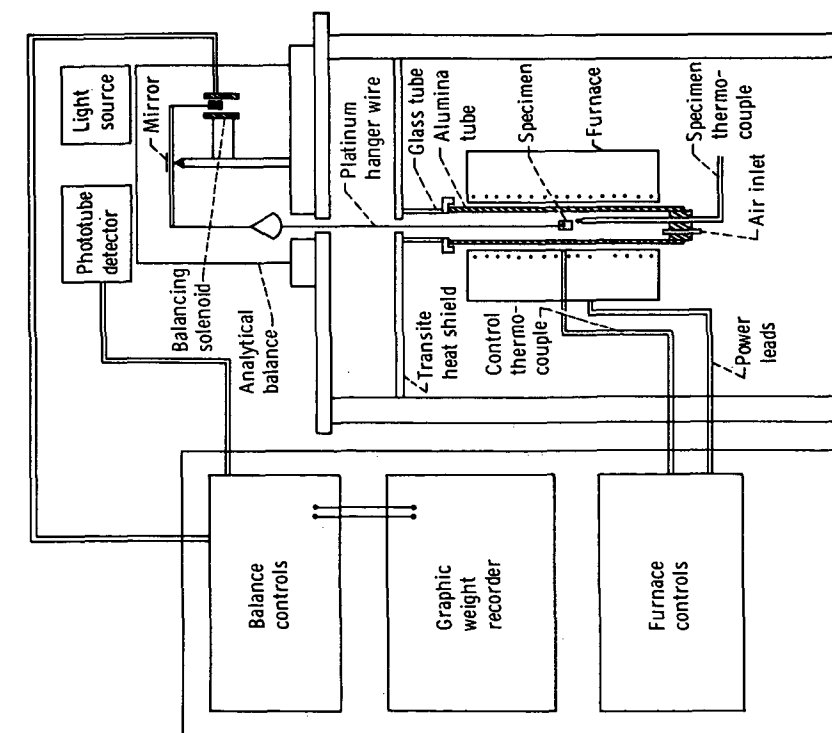


Figure 1. - Continuous weight-gain apparatus.

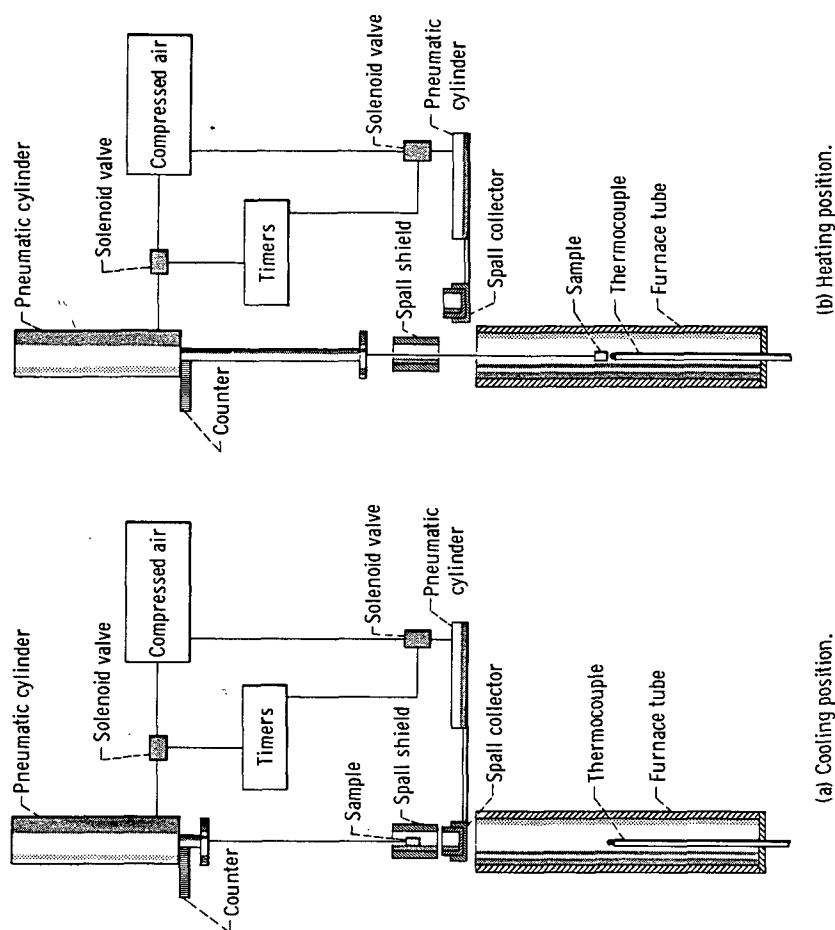


Figure 2. - Automatic cycling and spall collecting apparatus.

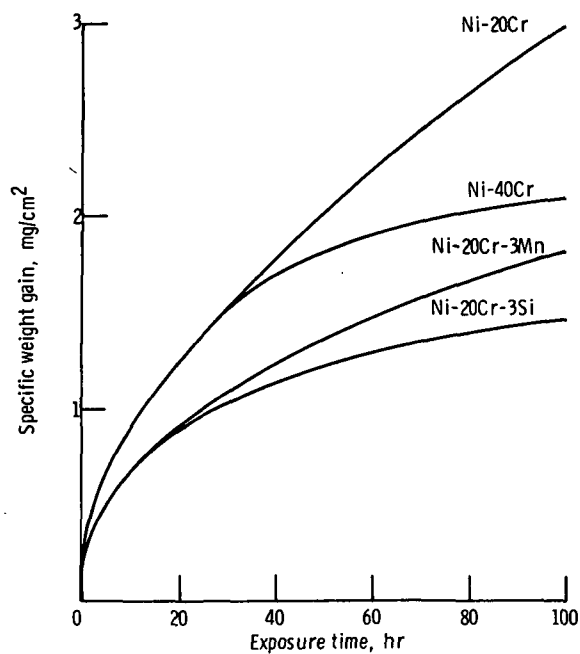


Figure 3. - Effect of composition on isothermal oxidation of nickel alloys at 1100°C in air.

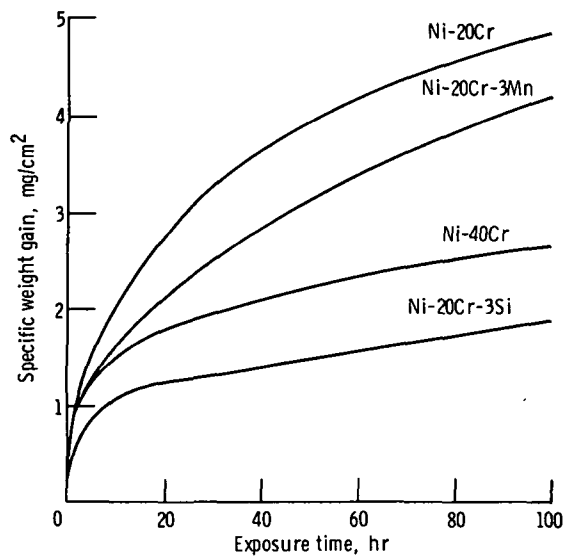


Figure 4. - Effect of composition on isothermal oxidation of nickel alloys at 1200°C in air.

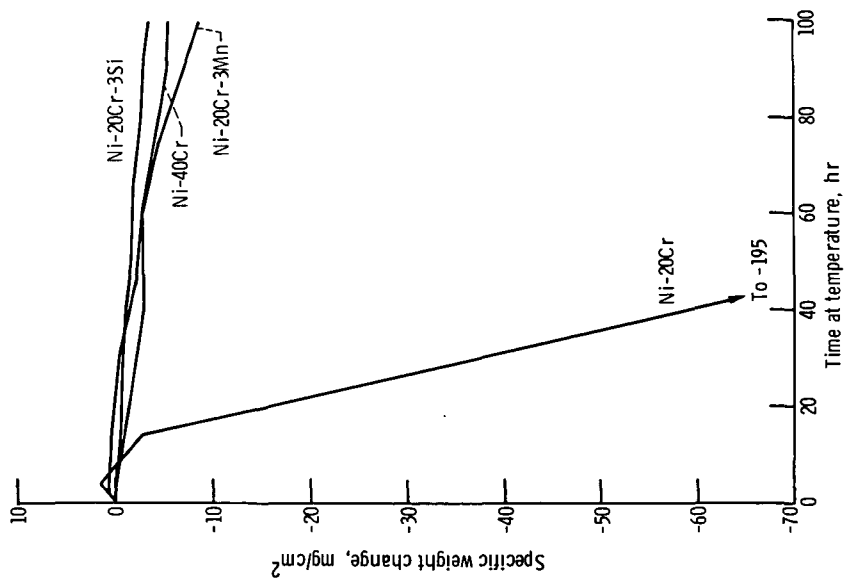


Figure 5. - Effect of composition on weight change of nickel alloys during cyclic oxidation at 1100°C. One hour at temperature per cycle; in air.

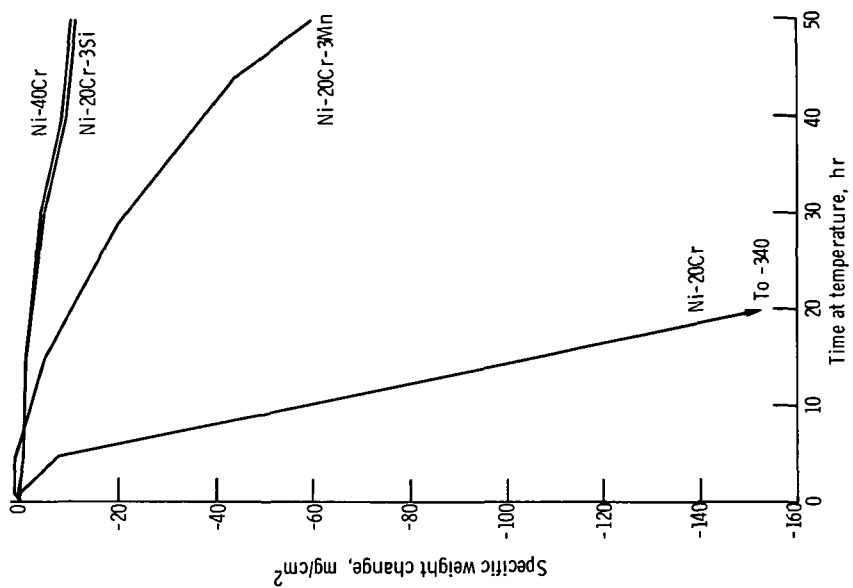


Figure 6. - Effect of composition on weight change of nickel alloys during cyclic oxidation at 1200°C. One hour at temperature per cycle; in air.



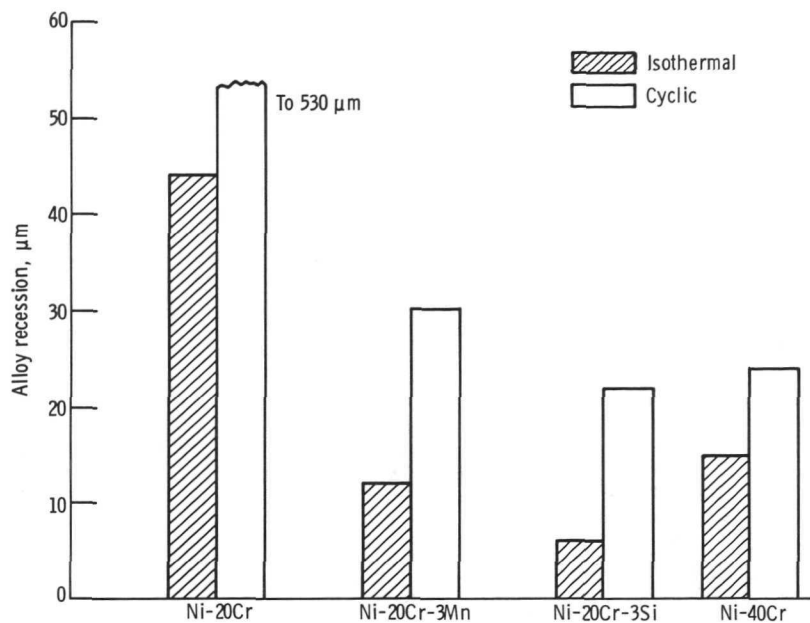


Figure 7. - Comparison of isothermal and cyclic oxidation behavior of nickel alloys at 1100° C as measured by alloy recession. All tests run in air for 100 hours at temperature.

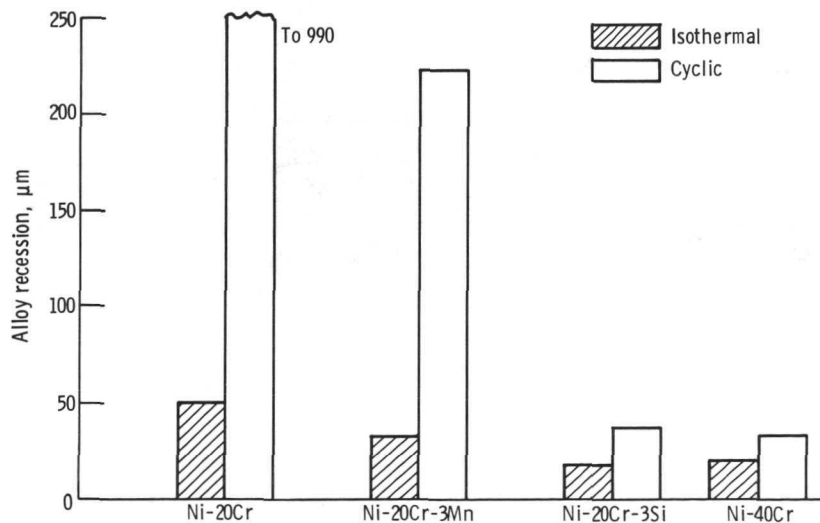
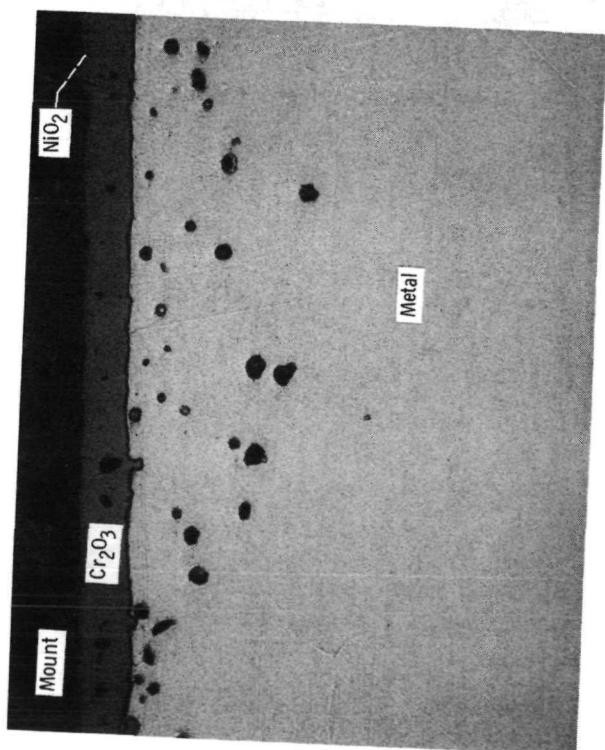
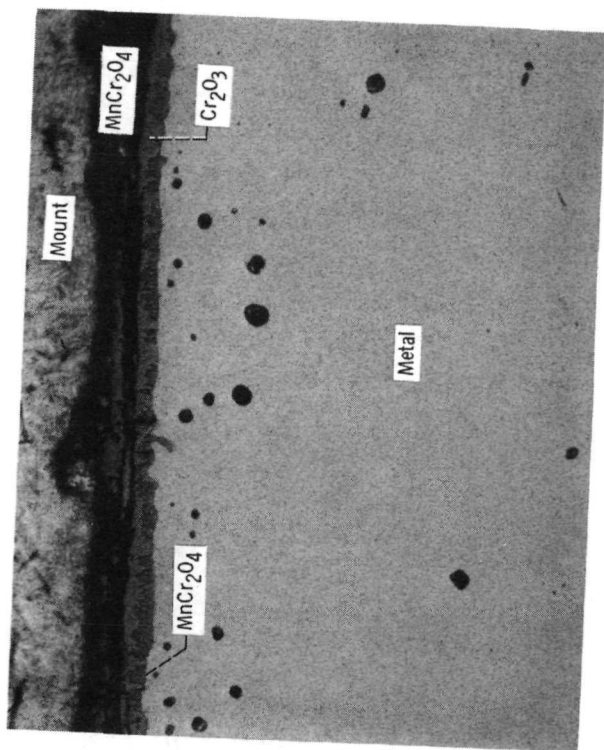


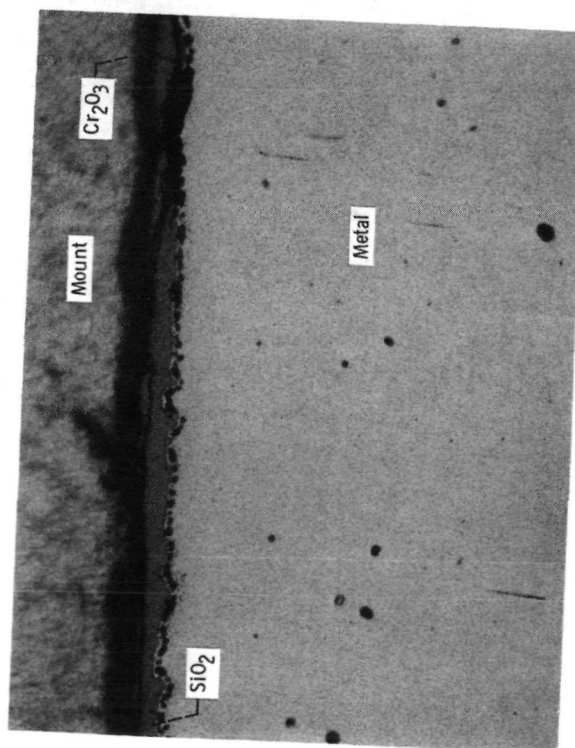
Figure 8. - Comparison of isothermal and cyclic oxidation behavior of nickel alloys at 1200° C as measured by alloy recession. All tests run in air for 50 hours at temperature cyclically and for 100 hours isothermally.



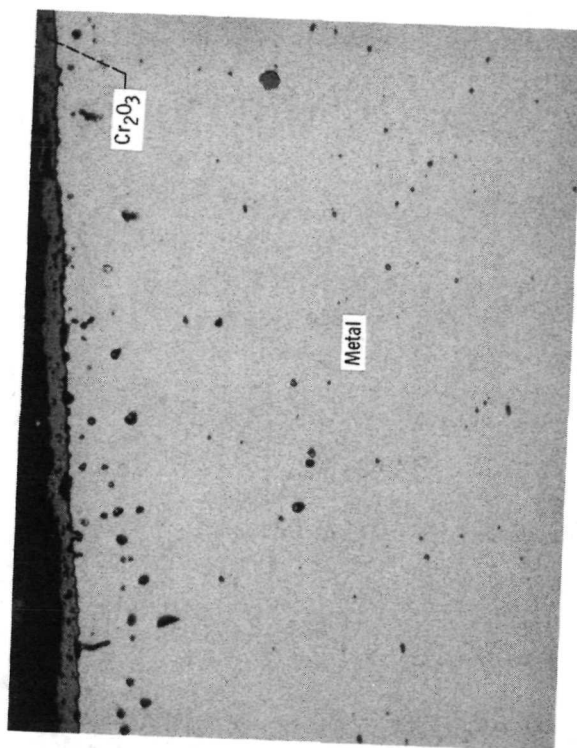
(a) Alloy, Ni-20Cr.



(b) Alloy, Ni-20Cr-3Mn.



(c) Ni-20Cr-3Si.



(d) Alloy, Ni-40Cr.

Figure 9. - Microstructures of nickel alloys oxidized isothermally at 1200°C in air for 100 hours. X250.

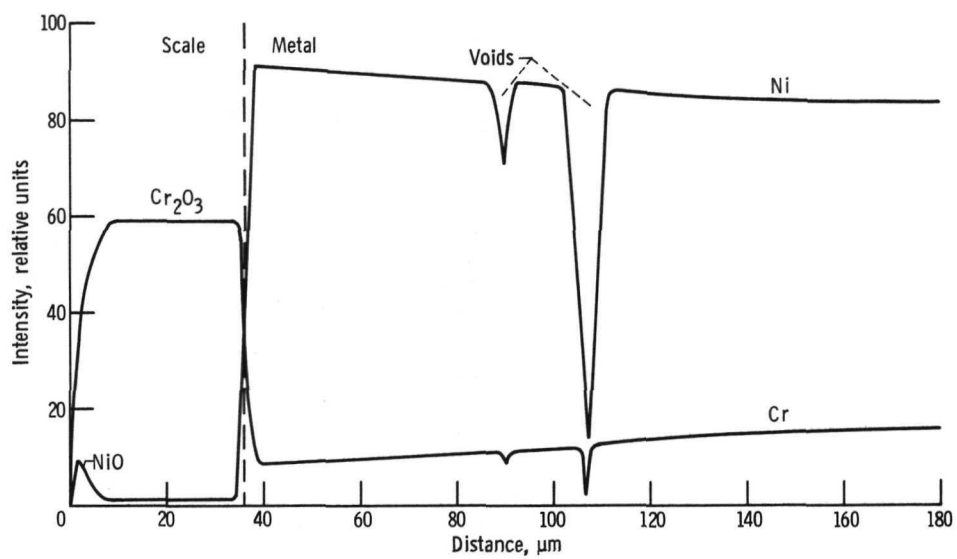
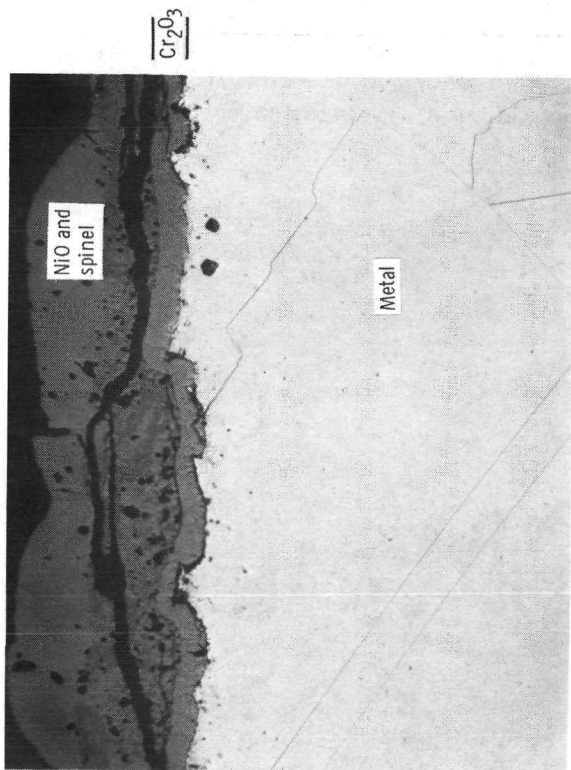
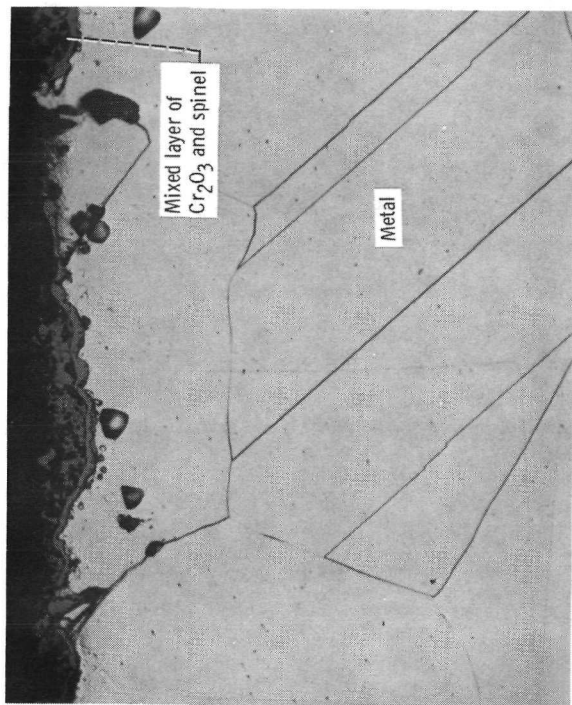


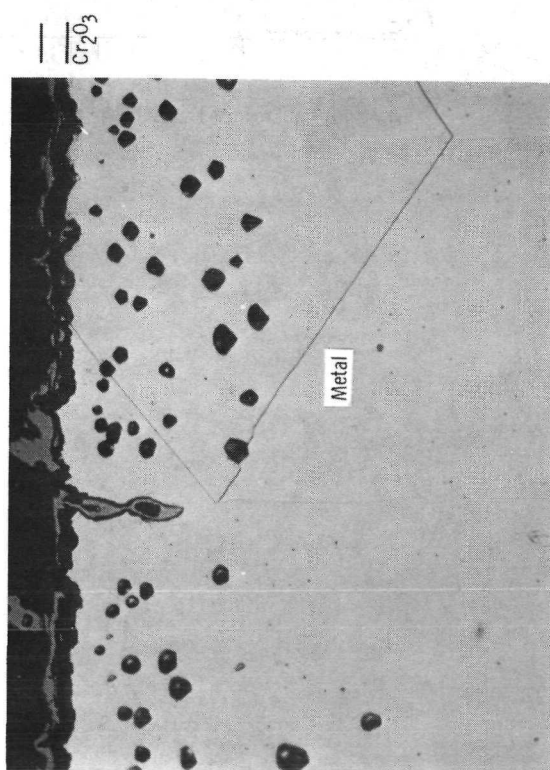
Figure 10. - Microprobe traces on Ni-20Cr after 100 hours of isothermal, air oxidation at 1200°C.



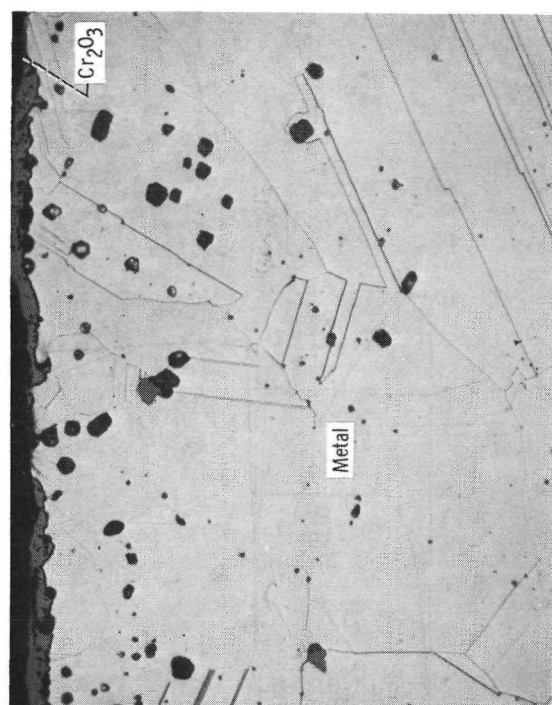
(a) Alloy, Ni-20Cr.



(b) Alloy, Ni-20Cr-3Mn.



(c) Alloy, Ni-20Cr-3Si.



(d) Alloy, Ni-40Cr.

Figure 11. - Microstructures of nickel alloys oxidized cyclically at 1200° C in air for 50 1-hour cycles. X250.

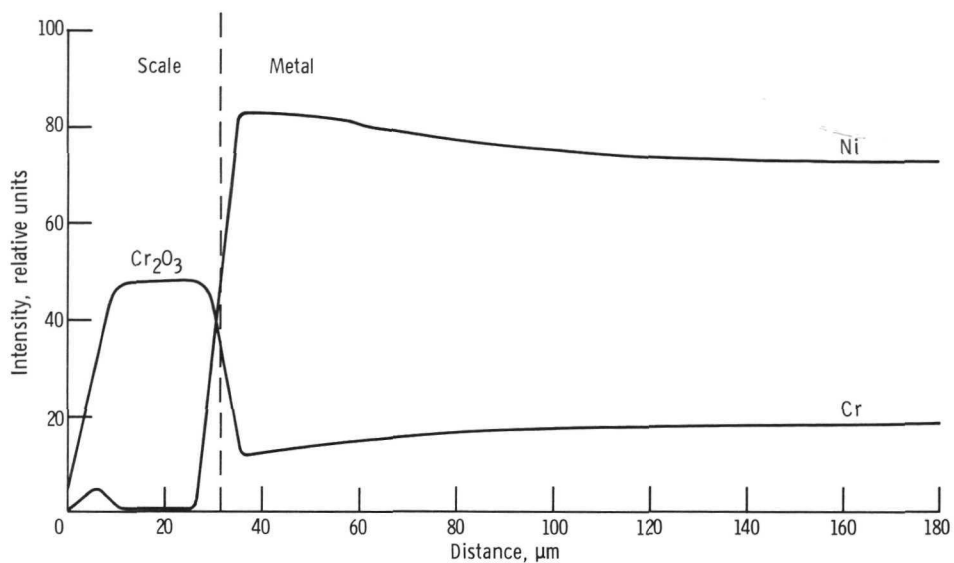


Figure 12. - Microprobe traces on Ni-20Cr after fifty 1-hour cycles of air oxidation at 1200<sup>o</sup> C.

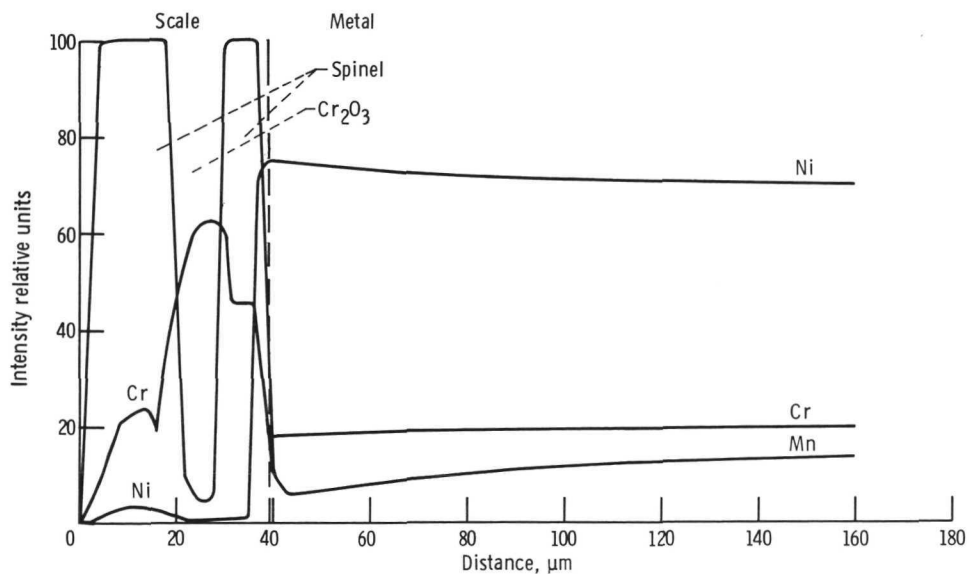


Figure 13. - Microprobe traces on Ni-20Cr-3Mn after 100 hours of isothermal, air oxidation at 1200<sup>o</sup> C.

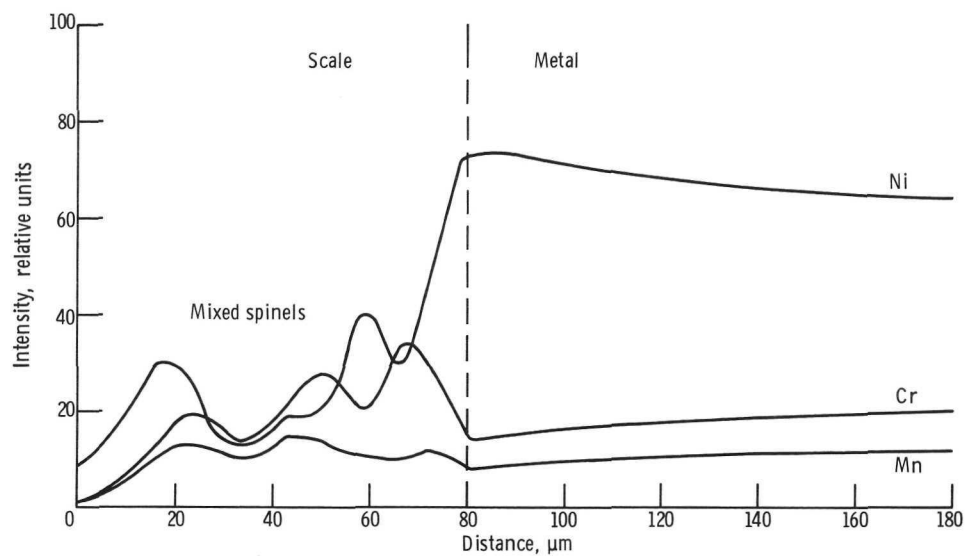


Figure 14. - Microprobe traces on Ni-20Cr-3Mn after fifty 1-hour cycles of air oxidation at 1200<sup>o</sup> C.

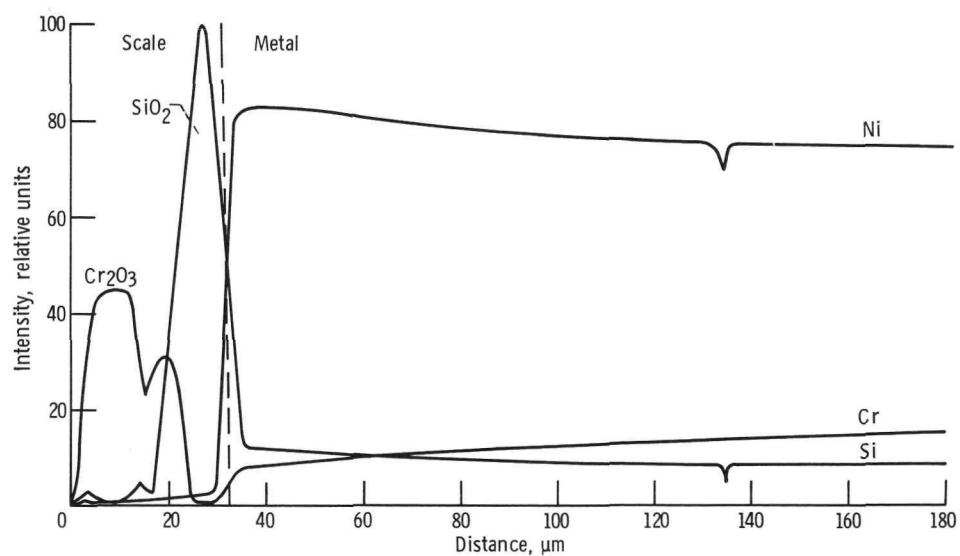


Figure 15. - Microprobe traces on Ni-20Cr-3Si after fifty 1-hour cycles of air oxidation at 1200<sup>o</sup> C.

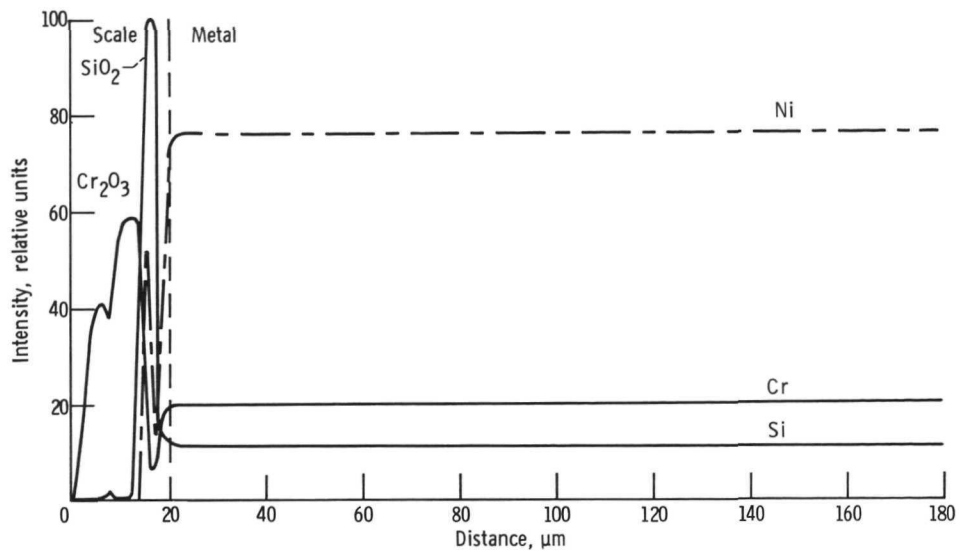


Figure 16. - Microprobe traces on Ni-20Cr-3Si after 100 hours of isothermal, air oxidation at 1200<sup>o</sup> C.

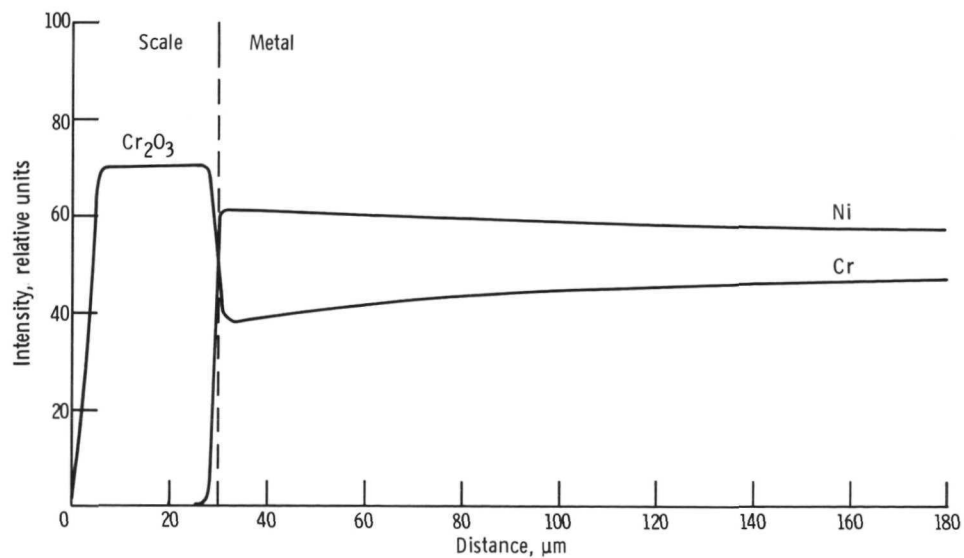


Figure 17. - Microprobe traces on Ni-40Cr after 100 hours of isothermal, air oxidation at 1200<sup>o</sup> C.

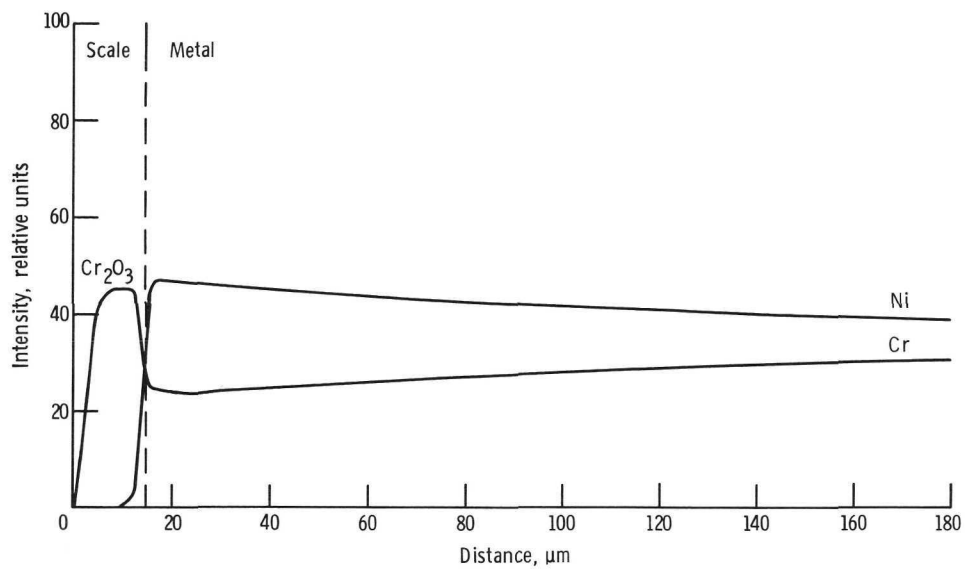


Figure 18. - Microprobe traces on Ni-40Cr after fifty 1-hour cycles of air oxidation at 1200<sup>0</sup> C.



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